SOME CHEMICAL ASPECTS OF UPPER-ATMOSPHERE RESEARCH

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INTRODUCTION

The chemistry of the upper atmosphere is a vast field abounding in research problems. The solar ultraviolet rays dissociate oxygen molecules, ionize nitrogen molecules, and provide the energy for many other photochemical processes. At upper-atmosphere densities which approach or surpass that of a good laboratory vacuum, chemical recombination reactions are slow and free radicals constitute large portions of the air. Processes such as the diffusive transport of the chemical enthalpy stored in the upper atmosphere add to the interest and complexity of the tenuous medium.

ATMOSPHERIC STRUCTURE AND COMPOSITION

It is of interest to examine briefly the structure of our atmosphere. We recall that density falls off by a factor of ten with roughly every ten miles of altitude increase. The hydrostatic equation and the perfect-gas law would tell a more accurate story, but we shall not require this.

Consider now (fig. 1) the variation of temperature with altitude.* Long-wave radiation emitted principally by H_2O and CO_2 keep the tropopause temperature low. Absorption of 2000 - 3000Å u. v. radiation by ozone warms the stratopause. Airglow radiations by the hydroxyl radical, OH (infra-red), atomic oxygen, O(5577Å),

*The temperature nomenclature in figure 1 originated with M. Nicolet. Although it is especially adaptable to the U. S. Standard Atmosphere, 1962, the nomenclature is not universally accepted.

forbidden transition), atomic sodium, Na (D-lines), etc. cool the mesopause. The thermosphere absorbs nearly all waves shorter than 2000 Å.

We shall be particularly interested in altitudes above 90 km. where the oxygen is largely dissociated. To most atmosphericists, the upper atmosphere starts here or perhaps at some lower altitude of special significance.

The first measure of atmospheric composition is the mean molecular weight (fig. 2), which is shown here as a function of altitude. Below 90 km., turbulent mixing and recombination win out over diffusive separation and photodissociation of oxygen, respectively, in maintaining practically a constant molecular weight. Above 90 km., the oxygen recombination is not fast enough to remove the atomic oxygen - even by the end of night.

Diffusive separation becomes increasingly effective and above 120 km. each species is settled out by gravity (according to its molecular weight) independently of the others. Moreover, turbulence is generally absent above 120 km.

Some important processes for the absorption of solar radiation are listed in figure 3. The Herzberg absorption cross-section is relatively small, but this provides enough atomic oxygen to maintain the small but important concentration of ozone in the stratosphere. On the other hand, absorption in the Schumann-Runge continuum is strong and these wavelengths are mostly absorbed in the thermosphere, thereby replenishing the supply of atomic oxygen above 90 km. altitude each day.

Some photochemical processes utilizing shorter wavelengths are also shown in figure 3.

CHEMICAL RELEASE EXPERIMENTS

Laboratory simulation of the upper atmosphere is generally difficult and rocket-borne experiments, usually backed up by ground-based equipment, are frequently essential to an atmospheric research program.

This paper will describe an experimental technique for measuring winds and other properties at night at altitudes greater than approximately 90 km. The technique complements the well-known sodium vapor trail technique which is applicable at twilight. Whereas the sodium method is based upon resonant scattering of the D-lines at twilight, the technique to be described utilizes a chemiluminescent gas trail whose behavior is observable at night.

The energy for the chemiluminescent gas reaction is derived from the chemical energy stored in the upper atmosphere in the form of atomic oxygen.

The relative abundance of species is shown (fig. 4) in relation to altitude. Dissociation, ionization, and diffusive separation (or"settling out" according to molecular weight) largely account for the relative abundances of the atmospheric species at various levels. Note, for example, that O is more abundant than N_2 above about 300 km. An important change of a different type takes place at a higher altitude. The exosphere, where (neutral) particles follow ballistic paths and practically never collide, has its base at about 550 km. At still higher altitudes charged particles predominate and the effect of the geomagnetic field is profound.

Let us return to the technique for measuring winds in the lower heterosphere, that is, above 90 km. The practicability of the chemiluminescence technique was demonstrated in 1956 by J. Pressman and others (ref. 1) of Air Force Cambridge Research Center in an experiment in which nitric oxide was released above 100 km. altitude and produced chemiluminescence which lasted for several minutes. Since that time Air Force Cambridge Research Center has conducted similar experiments with other chemicals, for example, ethylene, a mixture of sodium and thermite, carbon disulfide, and trimethyl aluminum. The most successful of these was trimethyl aluminum (ref. 2); above 100 km. altitude the duration of the glow was more than adequate for wind measurements. However, the preparation of a rocket payload of trimethyl aluminum is very hazardous and presents a serious safety problem to a group desiring to carry out routine upper-atmosphere measurements.

Figure 5 shows in greater detail the basis for the upper-atmosphere research technique of interest here. It should be noted that the chemical X may actually be a product of the initial reactions of the released chemical (say, trimethyl aluminum) with the ambient atomic oxygen. X is typically, although not necessarily, a monoxide such as NO or AlO. The latter can be produced directly by a thermite reaction (followed by rapid expansion into the near-vacuum above 100 km.).

If the bond energy of XO is less than 2.3 electron volts, the O_2 produced in the second reaction in figure 5 may be in an excited electronic state ($^1\Sigma_g^+$) leading to the emission of the Kaplan-Meinel bands (the visible ones of the "atmospheric bands," around 5380-7710Å).

Indeed, this may account for most of the radiation if the first reaction is extremely slow and if XO is released directly or is formed in another way (e.g., as an initial product - as noted above). Finally, the second reaction in figure 5 may leave X in an excited state and O_2 in the ground state; X could then radiate.

LANGLEY RESEARCH CENTER EFFORTS

The measurement of winds by cloud movement and triangulation from ground stations is generally straightforward. The inference of other atmospheric properties, however, requires an adequate mathematical theory which takes into account cloud dynamics, diffusion, chemical reaction, and radiation - all in proper relation to the ambient atmospheric medium.

Laboratory studies of reaction kinetics related to these experiments have been carried out by Professor H. I. Schiff at McGill University and Professor P. Harteck and Rensselaer Polytechnic Institute.

In 1960 the authors, at NASA's Langley Research Center, became interested in developing a workable chemical-release technique for studying the upper atmosphere. A chemical which would be a more efficient chemiluminescent agent and diffuse more slowly was sought. A combination of theoretical and practical considerations resulted in the selection of lead and bismuth for further study. At NASA's request, Harteck, Reeves, and Albers of RPI subsequently demonstrated the chemiluminescence of both lead and bismuth in the presence of atomic oxygen at a laboratory vessel pressure equivalent to about 75 km. altitude (unpublished results).

A bismuth vaporizer was developed at Langley and was based upon

reducing Bi_2O_3 with magnesium. Bismuth vapor released at 111 km. and at 121 km. over Wallops Island, Virginia in November, 1962 produced weak glows which were of one minute or less in duration. Photographic records were obtained, but these were not satisfactory for measuring winds.

The development of a PbO_2, Mg lead vaporizer was abandoned when two full-size payloads spontaneously ignited during the curing period for evaporating the binder solvent.

On the basis of laboratory studies which showed that sulfur vapor was chemiluminescent in the presence of atomic oxygen at low pressures, Harteck suggested releasing sulfur in the upper atmosphere in the form of CS_2. Both the Langley experiments and the Air Force Cambridge Research Center experiment of this type were surprisingly disappointing in yielding negligible chemiluminescence in the upper atmosphere.

The release of lead in the form of the organo-metallic tetra-alkyl compounds had been considered at Langley but abandoned because of the toxicity of the liquids. NASA interest in this was renewed by the Air Force Cambridge Research Laboratories experiment with trimethyl aluminum.

Thus, in the search for a satisfactory chemiluminescent agent, the Langley Research Center released tetramethyl-lead vapor trails in the lower heterosphere during two nighttime (early morning) experiments on January 22, 1964. In each experiment about 22 lbs* of liquid $Pb(CH_3)_4$ were carried aloft by the type of rocket shown in figure 6. The visible

*Since no heat was supplied to the liquid in advance of release, the vaporization was probably not complete.

chemical trail extended from an altitude of about 89 km. to 113 km. from the first release at 12:37 a.m. EST and from an altitude of 107 km. to 125 km. from the second release at 1:10 a.m. EST. The two trails are shown in time sequences in figures 7(a-c) and 7(d-f). The glow in each case persisted for approximately two minutes before fading beyond visibility.

Triangulation techniques are used to determine the trail positions in space from simultaneous photographs taken at widely separated and known locations (see ref. 3). For the present experiments, the photographic observations and the subsequent calculations for the wind velocities were supervised by Dr. Howard D. Edwards of the Georgia Institute of Technology under contract to the NASA (ref. 4). The wind measurements which resulted from these observations are shown in figures 8 and 9.*

The predominant feature of the wind profiles shown in figure 8 is the region of maximum wind speed which was measured near 110 km. on both flights. Above and below this altitude region, the wind speed is relatively small. These characteristics are consistent with other high altitude wind measurements, for example, the sodium trail measurements in references 5 and 6 and the tri-methyl aluminum trails in reference 7.

Another feature of figure 8 is the large change in the East-West component of the wind velocity at altitudes near 108 km. over the short time interval between the two trails. The figure indicates that the velocities varied from a westerly component of 60 to 80 mps to an easterly component of nearly 120 mps in 30 minutes. The North-South component also increased in magnitude by almost 50 percent during this time interval.

*The data used in figures 8 and 9 were the same; only the methods of graphical representation are different. Positive numbers correspond to wind components toward the North or East.

Inasmuch as the maximum errors associated with these measurements are estimated to be 10 mps, large variabilities in the wind components appear to be indicated by figure 8.

The hodograph type of plot of the wind data in figure 9 illustrates quite clearly the large variability in the wind speed and direction with altitude, particularly for altitudes up to wind maximum at 110 km. Several spiral-like variations spiral-like variations appear in figure 9 at the lower altitudes of the first release and indicate the existence of rather strong wind shears. The continuous spiraling change of direction with height accompanied by a gradually increasing wind speed until a maximum is reached close to 110 km. is typical of a number of other nighttime and twilight trail measurements reported in references 5, 6, and 7. The near midnight wind patterns over Wallops Island, Virginia, obtained from the present tetramethyl-lead vapor trails are thus quite similar in many respects to the twilight wind measurements obtained from sodium trails at the same location and to nighttime measurements at more southern latitudes.

CONCLUDING REMARKS

Further work in the chemical-release field is planned at Langley Research Center. This will probably include the consideration of other chemicals, engineering improvements, and the development of an adequate mathematical theory.

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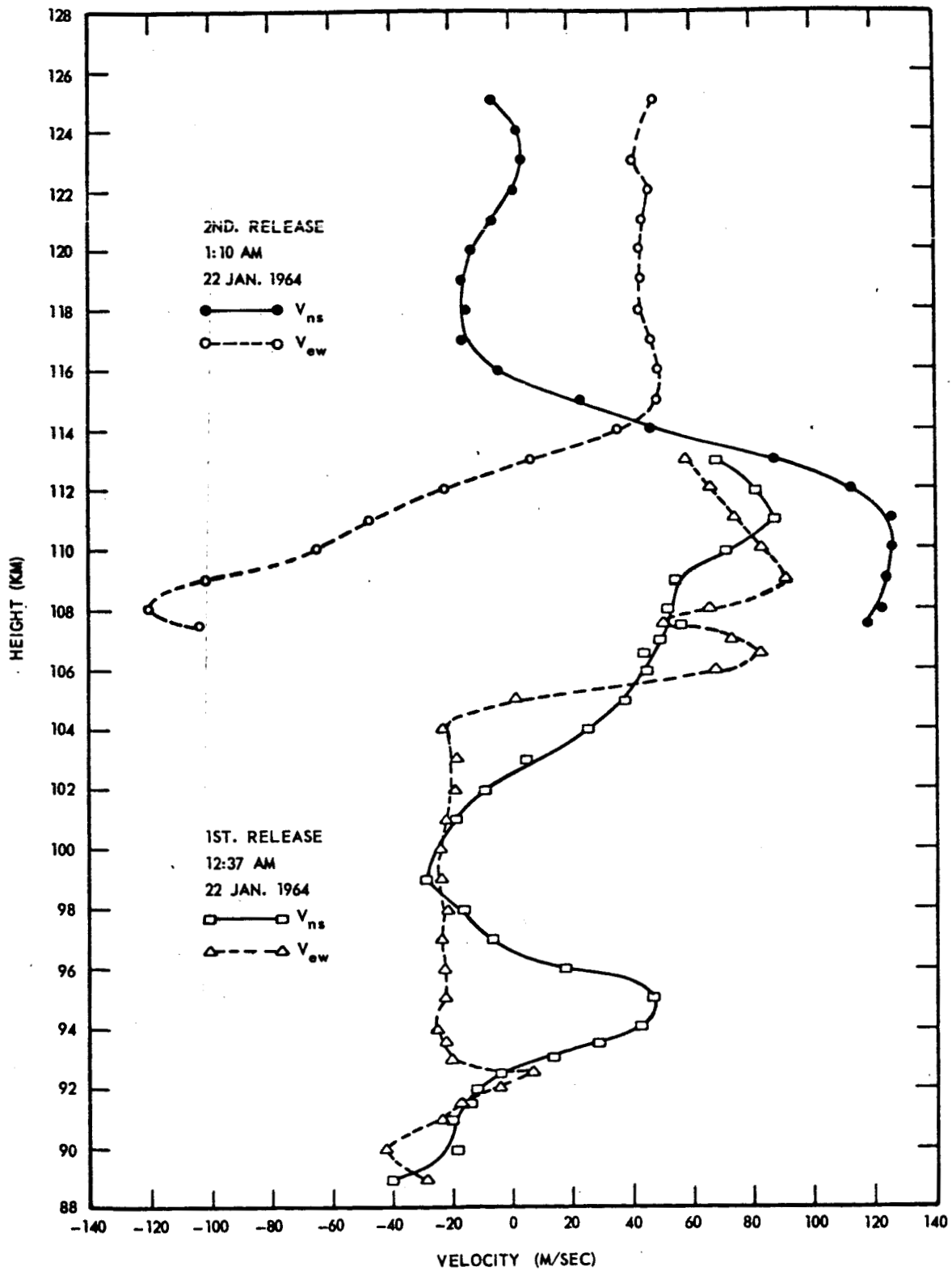

Figure 8.- North-South and East-West Components of the Wind Velocity

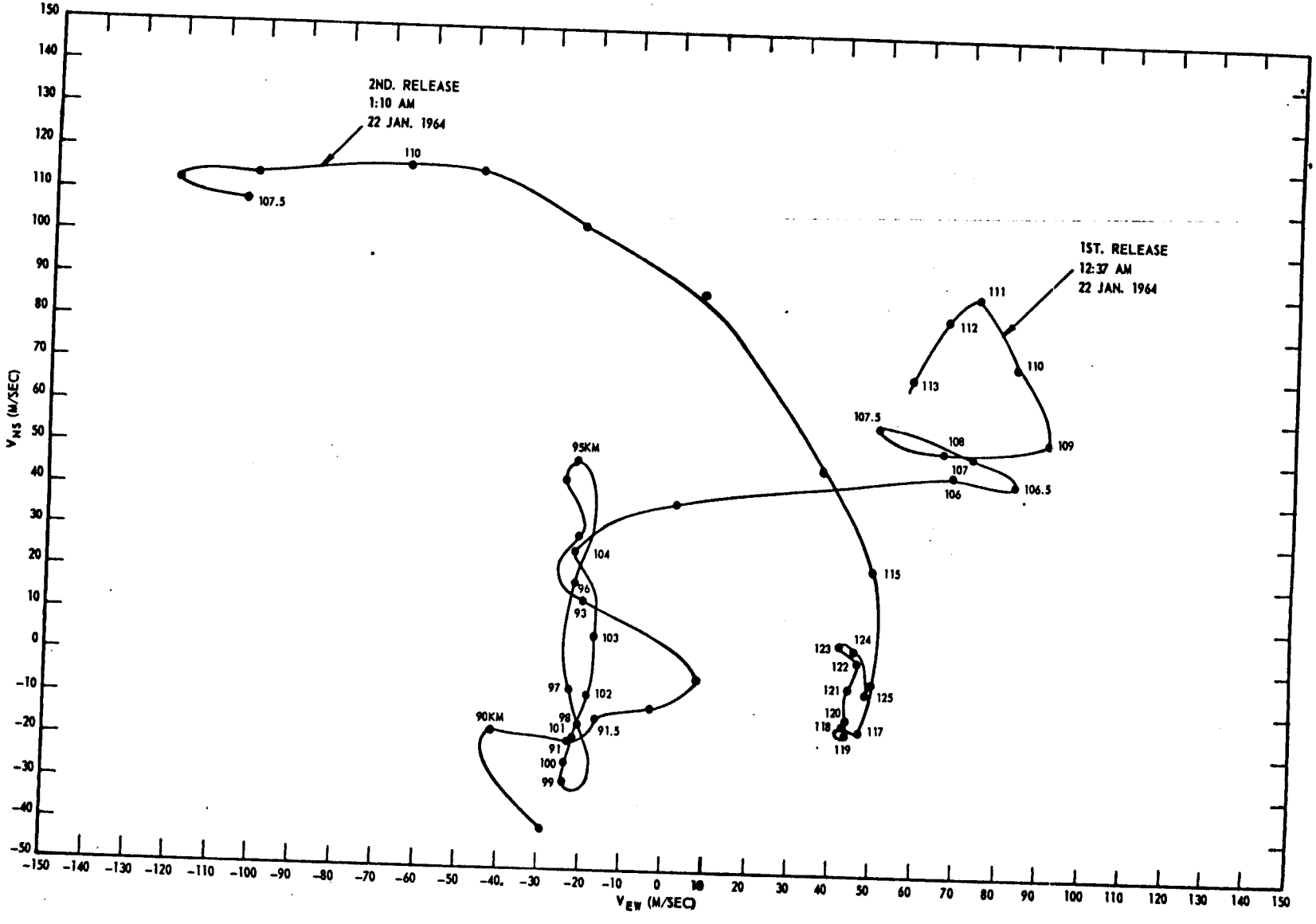

Figure 9.- Hodograph of Wind Velocity